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Scope and opportunities of using glycerol as an energy source

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ABSTRACT

Biodiesel is a promising fuel for diesel engines in wake of its renewable nature and environmental benefits. Biodiesel can be produced by different pathways; however, glycerol (or glycerin, glycerin) is a valuable by-product which is formed during this process. As mandates are being enforced by different government worlds over, the demand of biodiesel is likely to go up. With increased demand and production of biodiesel, significant quantity of glycerol shall be available. There is an urgent need to find alternative application area of glycerol so that viability of biodiesel industry can be sustained.

In the present study, the focus has been made on the various application areas of using surplus glycerol from biodiesel industries to make them more financially attractive. Amongst the different pathways of using glycerol as a source of energy; direct combustion, mixing with agricultural solid wastes and then burning, blending directly or indirectly with other fuels, hydrogen and hydrocarbon production from glycerol, etherification, etc. are prominent one. The requirement, advantages and limitations of each approach have also been evaluated in the study. Combustion of glycerol if not done properly would result in formation of acrolien which is highly toxic in nature and efforts should be made to use glycerol indirectly to produce energy (i.e. all the pathways expect the direct combustion and the solid fuel method). The production of hydrogen from glycerol via APR appears to be the best solution to the disposal problem since the hydrogen yield via APR is highest. Moreover the process occurs at lower pressure and temperature when compared to steam reforming, and it is a single step process. Etherification, tri-acetylisation, and blending have been found to be useful for improving the performance of automotives by facilitating proper and smooth combustion of fuel.

Contents

Abbreviations: MON, motor octane number; RON, research octane number; FT, Fisher–Tropsch; APR, aqueous phase reforming; MONG, matter organic non-glycerol; FAME, fatty acids methyl esters; PSA, pressure-swing adsorption

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1. Introduction

Biodiesel is becoming a promising fuel for diesel engines in wake of its renewable nature and environmental benefits. Biodiesel can be produced by different pathways; however, glycerol (or glycerin) is a valuable by-product which is formed during this process [1]. As mandates are being enforced by different government worlds over, the demand of biodiesel is likely to go up. With increased demand and production of biodiesel, significant quantity of glycerol shall be available. Glycerol has significant usage in pharmaceutical, cosmetic, soap and other industrial industries. However, with increased availability of glycerol, due to biodiesel production, the alternative utilization route need to be explored otherwise this will lead to its disposal problem and may also affect the economics of biodiesel industry [2]. Based upon the feedstock and the process selected, the Crude glycerol may also contain significant and variable amounts of excess methanol, water, catalyst, and a mixture of other organic material (soaps and unreacted fats and oils) collectively characterized as MONG (Matter Organic Non-Glycerol) and is therefore costly to refine into higher-grade glycerol [3]. As a consequence, crude glycerol market prices are low and falling and the biodiesel industry is challenged with viable options for this glut of glycerol [4]. Potential utilization of glycerol as a source of energy will not only alleviate its disposal problem but simultaneously, also enhance the profitability of existing biodiesel industries. Proper utilization of glycerol can reduce the costs of biodiesel production process up to 6.5% [1].

Glycerol presents desirable properties for combustion for heating purposes. There are various methods of utilizing crude glycerol as a source of energy. Currently most of by-product glycerol is sent to water treatment for digestion but this process is slow, expensive and has a low yield. Glycerol has been purified by distillation and used in both food and pharmaceutical industries. However, distillation is a costly process and the low price of glycerol makes it uneconomical. For large scale production the best option would be to use the by-product as a fuel directly; however, glycerol is a poor fuel which does not burn in either petrol or diesel engines [5].

2. Properties

2.1. Physical properties

Glycerol is a simple polyol compound. It is a colorless, sweet-tasting and having low toxicity, odorless and viscous liquid that is widely used in pharmaceutical formulations [6,7]. Glycerol is completely soluble in water and alcohol. It is slightly soluble in ether, ethyl acetate, and dioxane and insoluble in hydrocarbons. Glycerol has useful solvent properties similar to those of water and simple aliphatic alcohol's because of its three-hydroxyl groups. Glycerol contains three hydrophilic alcoholic hydroxyl groups, which are responsible for its solubility in water and its hygroscopic nature [8].

2.2. Chemical properties

Glycerol is a triol, i.e. a three carbon chain with hydroxyl group, one each on every carbon. The glycerol backbone is central to all lipids known as triglycerides [6,7]. The chemical formula of glycerol is $C_3H_5(OH)_3$. The structure of Glycerol is shown in Fig. 1.

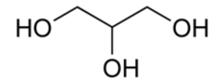


Fig. 1. Structure of glycerol.

Glycerol is a reactive molecule that undergoes all the usual reactions of alcohols. The two terminal primary hydroxyl groups are more reactive than the internal secondary hydroxyl group. Under neutral or alkaline conditions, glycerol can be heated to 250 °C without formation of acrolein. It is found that when heated at 280 °C, decomposition of glycerol starts via dehydration reaction to acrolein [8]. Hence, the reactions with glycerol are best carried out under alkaline or neutral conditions at 180 °C. Alkaline glycerol begins to dehydrate forming ether-linked polyglycerols. In addition, due to the presence of oxygen in their structure, it might reduce carbon monoxide and particulate matter emission from incomplete combustion [6].

At room temperature, glycerol rapidly absorbs water and when diluted with water, it is attacked by microorganism. On oxidation, glycerol yields variety of product depending upon the reaction conditions. With the use of mild oxidizing agent, it is possible to oxidize only one hydroxyl group to yield glyceraldehyde. These compounds may be considered very simple aldose and simplest ketoses respectively and mixture of two compounds obtained from glycerol as well as glyceraldehyde has been called glycerose. Nitric acid converts glycerol to glyceric acid $CH_2CHCHOHCOOH$. Some industrially important reaction products of glycerol include; mono, di, and tri esters of inorganic and organic acids, mono and diglyceride of fatty acids formed by transesterification of triglycerides, aliphatic and aromatic esters formed by reactions with alkylating agents, polyglycerols formed by the intermolecular alienation of water with alkaline catalyst, cyclic 1,2 or 1,3-acetals or ketals formed by the reaction with aldehyde or ketons respectively [9].

2.3. Structural properties

Glycerol is a highly flexible molecule forming both intra and intermolecular hydrogen bonds. There are 126 possible conformers of glycerol. In condensed phases, glycerol is characterized by a high degree of association due to hydrogen bonding. A first molecular dynamics simulation suggests that on average 95% of molecules in the liquid are connected. This network is very stable and very rarely, especially at high temperature, releases a few short living (less than 0.5 ps) monomers, dimers or trimers. In the glassy state, a single hydrogen-bonded network is observed, involving 100% of the molecules present. A highly branched network of molecules connected by hydrogen bonds exists in all phases and at all temperatures. The average number of hydrogen bonds per molecule ranges from about 2.1 in the glassy state to 1.2 in the liquid state at high temperature, with average activation energy of 6.3 kJ/mol required to break the hydrogen bond. Crystallization, which occurs at 291 K, cannot be directly achieved from the liquid state but requires special procedures. Due to the existence of such an extended hydrogen bonded network, the viscosity and the boiling point of glycerol are unusually high. Glycerol readily forms a super-cooled liquid which, by lowering the temperature undergoes at about 187 K transition to a glassy state whose nature has been the subject of a number of investigations. Remarkably, a recent single-molecule analysis has revealed a foam-like structure for glycerol at temperatures above the glass transition point (Tg, 190 K) comprising pockets of fluid isolated from one another by glass-like regions, which retain their distinct dynamics over surprisingly long timescales [9]. The various physico-chemical properties of Glycerol have been highlighted in Table 1.

3. Source of raw glycerol

Apart from biodiesel industry, there are other sources of glycerol as well which includes soap industry. The latter is

Table 1
Various physico-chemical properties of glycerol (at 20.1°C) [10].

1	Molecular weight	92.09
2	Melting point	18.17 °C
3	Boiling point(760 mm Hg)	290 °C
4	Density (20 °C)	1.261 g/cm3
5	Vapor pressure	0.0025 mm Hg at 50° C 0.195 mm Hg at 100 °C 4.3 mm Hg at 150 °C 46 mm Hg at 200 °C
6	Refractive index	1.474
7	Surface tension	63.4 dyne/cm at 20 °C (100% glycerol)
8	Compressibility (28.5 °C)	2.1 × 10 MPa
9	Viscosity	1499 c.p. at 20 °C (100% glycerol)
10	Specific heat	2.42 J/gm at 26 °C (99.94%glycerol)
11	Heat of vaporization	21060 cal/mole at 55 °C 18170 cal/mole at 195 °C
12	Heat of formation	159.6 Kcal/gm mole
13	Heat of combustion	1662 KJ/mole = 18.05 MJ/kg
14	Heat of fusion	18.3 KJ/mole
15	Thermal conductivity	0.29 w/°K
16	Flash point	177 °C
17	Fire point	204 °C

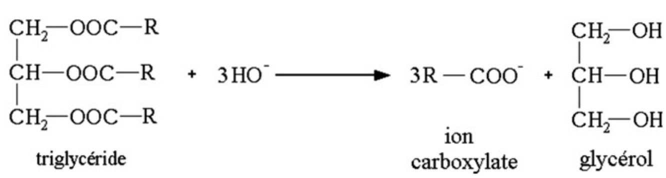


Fig. 2. Saponification of triglyceride.

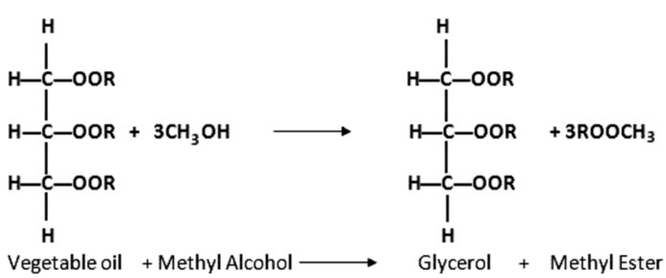


Fig. 3. Transesterification reaction.

traditional, while the former is nascent. In the soap industry, the triglycerides are saponified in the presence of alkali to produce alkali salts of free fatty acids i.e. soap and raw glycerol. The process is shown in Fig. 2.

On the other hand, biodiesel is produced through the transesterification of triglycerides (fats, oils, or lipids) into FAME in the biodiesel industry. The transesterification process is shown in Fig. 3.

During this process, the triglyceride raw material reacts with an alcohol (almost always methanol) in the presence of either a base catalyst (typically sodium or potassium hydroxide) or an acid catalyst (depending upon the method practiced) to produce biodiesel. On a molar basis, one mole of glycerol is produced for every three moles of FAME, and, approximately 10% of the initial reactants are converted to glycerol. The composition of crude glycerol can vary depending upon the type of feedstock used, method involved, storage, impurities, etc. The percentage composition of raw glycerol may include pure glycerol (25–85%), methanol (upto 25%), water (2–5%), ash (1–9%) and salt, soap, etc. in small quantities [3,8,11,12]. Although raw glycerol is unfit for its utilization, several new cost effective and easy to perform methods have been devised for its utlization.

4. Glycerol as a source of energy:

There are different strategies of using glycerol as a energy source and these are highlighted in subsequent sections.

4.1. Direct combustion of crude glycerol

Crude glycerol can be burned directly. However, the combustion of glycerol has been challenging because of technical, safety, and cost obstacles. By nature, glycerol has a high viscosity, high auto-ignition temperature and low heating value. These properties make flow of glycerol difficult in a burner, hard to ignite, and even more challenging to maintain a flame. Due to these reasons, acrolein is produced during the combustion of crude glycerol [4].

Acrolein production is due to unstable combustion leading to low temperature and too short residence time of combustion products in the high-temperature zone. It has been found that this carcinogenic agent decomposes in full at high temperatures and could not be detected by the methods used. It is also found that acrolein is not produced during glycerol combustion at a temperature of 1000 °C [8]. However, ash content (in the form of any salt, soap etc.) may choke the burners after sometime. Although not an ideal fuel, waste glycerol may be used in boilers to produce process steam and co-generate electricity with the added advantages of optimizing energy integration, eliminating transportation costs, and displacing the need for fossil fuels [3].

Till 2006, glycerol (derived as a by-product) was blended with fuel oil and burnt as a fuel. However, a new European directive (waste incineration directive) has put an end to this recycling because of fear of pollution from unburnt combustion products [5]. Also, the patent-pending burner system developed by DEC-NCSU uses a novel spray atomization swirl burner architecture that overcomes technical and safety issues. This includes a unique approach to pre-heat the combustion chamber, maximize heat and radical retention, and carefully mix the air and fuel flows. The system is also extendable to any liquid fuel having an ambient viscosity up to a few hundred centistokes [4].

4.2. Solid fuel

Solid fuel derived from either dried durian shell or bagasse and glycerol can be used as an alternative fuel based upon their energy contents. The optimum weight ratio for the mixture is roughly 65:35 for both durian shell and bagasse based glycerol solid fuel. Low concentration of acrolien is expected in the exhaust gases if the combustion takes place in an open environment. In addition, the strength of solid fuel may be improved by use of binding material [13].

4.3. Blending

Blending with other fuels may also be done. The various fuels which can be blended are propanol, propanediol, ethanol and gasoline. The amount of glycerol that could be successfully blended with gasoline was found to vary widely depending on the amount of n-propanol amphiphile present. Analyses for primary fuel properties of glycerol, propanediol, propanol, ethanol, and gasoline blends suggest that certain blends could be used as spark ignition fuels [14,15]. The comparison of different blends of glycerol with other blends is summarized in Table 2.

4.4. Producing hydrogen from glycerol

There are different methodologies which can be adopted for production of hydrogen from glycerol. These are deliberated in subsequent sections.

Table 2
Comparative assessment of different glycerol blended fuels with other fuels. [14].

Sample	Composition (vol%)	Energy value (MJ/kg)	Octane number	
			MON	RON
1	Glycerol (6%), propanol (60%) and gasoline (34%)	33.25	> 100	N
2	Ethanol (30%), glycerol (30%) and propanediol (40%)	20.83	> 100	N
3	Propanol (40%), gasoline (20%) and propanediol (40%)	28.63	> 100	N
4	Ethanol (14%), gasoline (76%) and propanediol (10%)	38.05	84.0	93.9
5	Propanol (33%), ethanol (33%) and propanediol (34%)	25.60	> 100	N

N: not measured.

Table 3
Reactions involved in steam reforming glycerol [16].

				Energy change (kJ/mol)
1	$C_3H_8O_3+3H_2O$	↔	$7H_2+3CO_2$	+128
2	$C_3H_8O_3$	↔	$4H_2+3CO$	+250
3	$C+H_2O$	↔	$CO+H_2$	+131
4	$CO+H_2O$	↔	CO_2+H_2	−41
5	$C+2H_2$	↔	CH_4	−75
6	$CO+3H_2$	↔	CH_4+H_2O	−206
7	CO_2+4H_2	↔	CH_4+2H_2O	−165
8	$C+CO_2$	↔	2CO	+172

4.4.1. *By the means of steam reforming*

Steam reforming of carbohydrates, like glycerol, is thermodynamically favorable at lower temperatures than hydrocarbons, so the steam reforming of oxygenates can take place at lower temperatures because it is more exothermic [5]. Table 3 shows the reactions involved in the steam reforming of glycerol [5,16]

Glycerin steam reforming for hydrogen production has been conducted over cheaper catalysts like Ni-based catalysts. It has been found that Ni/MgO is the best one as compared to Ni/TiO2 and Ni/CeO2 [17].

4.4.2. *Production of hydrogen via aqueous phase reforming (APR)*

The APR process efficiently generates easily purified hydrogen by the reaction of glycerol with water to form carbon dioxide and hydrogen as per the following equation:

$$C_3H_8O_3+3H_2O \rightarrow 3CO_2+7H_2$$

This reforming reaction takes place over a catalyst in a single reactor. The gas stream leaving the APR can be utilized directly as a high energy fuel for internal combustion engines, gas-fired turbines or solid oxide fuel cells. The process for the production of hydrogen from glycerol is cost effective since it generates hydrogen without the need to volatilize water, which represents a major energy saving. It occurs at lower temperatures (200–250 °C) and pressures above the bubble point of water (15–50 bar), where the water–gas shift reaction is favorable, making it possible to generate hydrogen with low quantities of CO in a single chemical reactor. At such conditions, the hydrogen rich effluent can be purified effectively using pressure-swing adsorption (PSA) technology. The operating low temperatures, also minimizes the undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures. The raw water-soluble glycerol waste from biodiesel production is an ideal feedstock for the APR process. At the reaction temperatures investigated, CO concentrations were below 300 ppm, and this method is particularly well suited for generating hydrogen on demand in a compact and highly efficient single-step reactor. Operating temperatures are one-third of those in other processes, with the generation of 10 times more hydrogen per g of catalyst. The reaction of glycerol has been conducted over a precious metal catalyst like Platinum supported on g-alumina MgO and ZrO_2 presented good potential activity with high production of hydrogen and low concentration of undesired hydrocarbons. Subsequent investigations have revealed that a range of catalyst compositions are active for the generation of hydrogen by aqueous phase reforming of oxygenated compounds, in particular inexpensive nickel-based materials and selective APR catalysts. Furthermore, it has showed that the nature of the support influences the catalytic performance on glycerol reforming. Importantly, the gas stream leaving the APR is within the required feed pressure range for the PSA unit (between 16 and 40 bar). Accordingly, the PSA unit does not need an expensive and energy-consuming compressor to provide the necessary feed pressure. This results in lower capital costs and increased energy efficiency [9,18–20].

4.5. *Production of hydrocarbon fuels via APR*

Liquid alkanes can be produced directly from glycerol in a two-bed reactor system using an integrated process consisting of APR followed in a single reactor by Fisher–Tropsch (FT) conversion. Glycerol can be converted in this way to synthesis gas at high rates and selectivity at temperatures between 225 and 335.1 °C, according to equation.

$$C_3O_3H_8 \rightarrow 3CO+4H_2$$

Operation at low temperatures provides the opportunity to couple this endothermic glycerol conversion with the exothermic FT synthesis to produce liquid transportation fuel from aqueous glycerol solutions via an integrated process. In particular, either glycerol conversion or FT synthesis can be carried out effectively under the same conditions in a two-bed reactor system. This integrated glycerol-based process improves the economics of "green" FT synthesis by reducing costs, eliminating the need of a biomass gasifier, by reducing the size of the synthesis reactor, by producing an undiluted synthesis gas stream and by eliminating subsequent cleaning steps. In addition, the process can produce synthesis gas of varying H_2–CO composition, thus eliminating the need for a water–gas shift reactor and allowing for the use of FT catalysts that operate at different H_2:CO ratios. Synthesis gas production and clean-up are indeed the critical steps in producing liquid alkanes from biomass and account for more than 50% of the total costs of producing these by "green" FT synthesis. Hence, for example, conversion of glycerol over a 10 wt% Pt–Re/C catalyst with a Pt:Re ratio of 1:1 produces a synthesis gas stream suitable for Fischer–Tropsch synthesis (H_2:CO between 1.0 and 1.6) from concentrated glycerol feed solutions at low temperatures (275 1C) and pressures up to 17 bar, where incomplete vaporization of the glycerol feed occurs (Figure 2.9). The synthesis gas produced in the first process is fed directly into the second reactor consisting of a 2.9 wt% Ru–TiO_2

catalyst bed whose intermediate value of w (50_1016m_1) leads to optimum C51 selectivity. This combined process produces liquid alkanes, with SC51 between 0.63 and 0.75 at 275 1C and pressures between 5 and 17 bar, with more than 40% of the carbon in the products contained in the organic liquid phase at 17 bar. The aqueous liquid effluent from the integrated process contains between 5 and 15 wt% methanol, ethanol and acetone, which can be separated from the water by distillation and reused, or recycled for conversion to gaseous products. Importantly, the coupling of glycerol conversion to synthesis gas and FT synthesis leads to synergies in the operations of these processes, such as avoiding the highly endothermic and exothermic steps that would result from the separate operation of these processes; eliminating the need to condense water and oxygenated hydrocarbon by-products between the catalyst beds; allowing operation at higher pressures (i.e., 17 bar), at which synthesis gas production over Pt–Re/C is decreased and the production of liquid by-products increased; and causing an increase in selectivity to C51 hydrocarbons.The primary oxygenated hydrocarbon intermediates formed during conversion of glycerol to synthesis gas are ethanol, acetone, and acetol; all have positive effects on the FT synthesis step. In particular, water, ethanol and acetone have a slightly positive effect, such as increasing the selectivity to C51 hydrocarbons (SC51) by a factor of 2 (from 0.30 to 0.60). Acetol can participate in Fischer–Tropsch chain growth, forming pentanones, hexanones and heptanones in the liquid organic effluent stream lar weight distributions for experiments that combined glycerol conversion with Fischer–Tropsch synthesis, and these distributions exhibit deviations from the kinetics of the Anderson–Schulz–Flory (ASF) chain growth model similar to the FT experiments, indicating a-olefin re-adsorption effects. The oxygenated hydrocarbon by-products from glycerol react over the Ru–TiO_2 bed, most likely by entering into chain growth. The C51 selectivity, selectivity to pentanones, hexanones and heptanones in the organic liquid, and the conversion of CO for combined glycerol conversion with Fischer–Tropsch synthesis at 11 and 17 bar, are all higher than those at 5 bar, despite the fact that synthesis gas production from glycerol is decreased at these elevated pressures. The more favorable FT conditions (i.e., higher pressure) are more important to the integrated process than the synthesis gas production rate [9,21–23].

4.6. Utilization of glycerol to produce triacetyl-glycerol

The triglyceride 1,2,3-triacetoxypropane is more generally known as triacetin and glycerol triacetate. It is the trimester of glycerol and acetic acid. Triacetin can also be used as a fuel additive as an antiknock agent which can reduce engine knocking in gasoline, and to improve cold and viscosity properties of biodiesel. It can also be used as an additive in propulsion system of rockets. High selectivity and high conversion rate for producing triacetylglycerol from the by-product glycerol can also be obtained using a two-step method. The first step is production of glycerol via transesterification. The second step is the esterification of glycerol with acetic acid can be carried out over resin and zeolites and Amberlyst-35 been found to be an excellent catalyst [24].

4.7. Etherification of glycerol

It is a promising process that can convert glycerol to mono, di and tri-*tert*-ether of glycerol. These chemicals are useful as diesel fuels due to their good blending property and high cetane number. In addition, due to the presence of oxygen in their structure, it might reduce carbon monoxide and particulate matter emission from incomplete combustion [6,7,25].

5. Conclusion

There are many pathways of utilizing glycerol as energy source and apperantly, the most hassle free way is to burn the crude glycerol directly. However, unfortunately it is very hazardeous because of the formation of acrolien in high quantity during its direct combustion. Moreover the ash produced due to combustion may also choke the nozzles. However, combustion at high temperature can alleviate the formation of acrolien. Cakes made using a mixture of agricultural waste and crude glycerol, if used as a solid fuel will casuse the problem of ash disposal. Blending is a very good option for proper utilization of glycerol, however, the blending should be done in such a manner that the raw glycerol can be disposed in a sustainable manner. Since glycerol is a carbohydrate, blending means oxygenating the fuel and the particulate and NOx can be reduced and octane number can be improved. After etherification, the glycerol becomes a good cetane improver for diesel fuel. Etherified glycerol also aids in reducing carbon monoxide and particulate emission. Hydrogen can also be produced from glycerol. APR is much better than steam reforming for hydrogen prouction as APR is a single step process and has relatively high yield per gram of catalyst. Further production of hydrocarbon fuels via APR is even more attractive method of glycerol utilization. The production of hydrocarbons can also be made specific by the means of catalysis. Hence the hydrocarbon fuel from glycerol via APR can have very high percentage of one type of hydrocarbon based upon specific requirement. These hydrocarbons are poised to perform better than the petroleum gasoline, and eliminate the problem of cold starting. Triacetin is another material derived from the glycerol, which can be used as an additive in propulsion fuel, as an antiknock agent in gasoline IC engines which can reduce engine knocking and to improve cold and viscosity properties of biodiesel. To be on the safer side, glycerol should be utilized to produce energy, indirectly (i.e. all the pathways expect the direct combustion and the solid fuel method). Unfortunately except direct combustion and solid fuel method, all the other pathways require purification of crude glycerol. Nevertheless, new technologies for easy purification of raw glycerol have been developed which would make the above methods econonomically feasible.

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